

Polymer-Boundary Surface Interactions and Bilayer Curvature Elasticity.

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(received 14 April 1992; accepted in final form 21 October 1992)

PACS. 82.70 – Disperse systems.

PACS. 05.20 – Statistical mechanics.

PACS. 61.25H – Macromolecular and polymer solutions (solubility, swelling, etc.); polymer melts.

Abstract. – The free-energy contribution of a polymer interacting with a bounding surface of a general shape is obtained exactly through a multiple-scattering expansion. Two extreme cases of the polymer interacting with a surface are considered, *viz.* an ideal polymeric chain sterically excluded from the vicinity of the surface and an ideal polymeric chain adsorbed to the surface. In both cases the thermodynamic properties of the system are obtained in the form of a convergent expansion in powers of the local principal radii of curvature of the bounding surface.

Elastic properties of fluid bilayer membranes of surfactant molecules are essential for the understanding of self-assembly processes in biological systems in general, as well as for shape transformations, to which vesicles can be subjected by varying the external constraints, in particular [1]. The bilayer elasticity is standardly approached through an expansion of the free energy in terms of local radii of curvature up to the second order [1]. It is interesting in this context to assess the consequences of adding a flexible polymeric chain to the bathing solution, for the properties of the curvature expansion of the free energy. Indeed the problem has recently received a lot of attention [2] and the emerging picture is that even in the case of polymer adsorption the harmonic curvature expansion of the free energy is preserved. The theoretical approach thus far [2] has been limited to considerations of fixed geometries (*e.g.*, spherical or cylindrical), that have fixed radii of curvature. The polymer (with excluded-volume interactions) was modelled either in the framework of the Cahn-de Gennes theory or of the modified scaling theory with added (contact) polymer-surface interactions. The results were obtained in the form of a (constant) curvature

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expansion of the surface free-energy density, where the elastic constants were functions of the contact polymer-surface interaction energy [2].

In this contribution we will set forth an approach, based on the Balian-Duplantier [3] multiple surface scattering Green's function formalism used recently in the analysis of the related charged-surface problem [3], that will permit us to obtain the expansion of the free energy in terms of local curvatures without any need to specify the underlying global geometry of the bounding surface. We will thus be able to derive an expansion of the free energy even if the principal curvatures vary along the bounding surface. We will use this formalism to derive the free-energy local-curvature expansion for two extreme cases of the polymer interacting with a surface, *viz.* an ideal polymeric chain depleted from the vicinity of the surface (steric exclusion) and an ideal polymeric chain weakly (in the sense of ref. [4]) adsorbed to the surface.

We limit our discussion to the consideration of an ideal polymer interacting with a single bounding surface whose curvature is a function of the surface coordinates. The bare Helfrich curvature energy [1] of the surface has thus the form

$$\mathcal{F} = \frac{1}{2} K_c \int_{(S)} dS \left(\frac{1}{R_\omega} - \frac{1}{R_0} \right)^2 + \bar{K} \int_{(S)} dS \frac{1}{R_1 R_2}, \quad (1)$$

where R_1, R_2 are the two principal local radii of curvature, $1/R_\omega = (1/2)(1/R_1 + 1/R_2)$ is the mean local curvature, R_0 is the spontaneous curvature, K_c is the elastic modulus and \bar{K} is the Gaussian-curvature modulus. The interactions between the polymer and the bounding surface we consider here will be assumed to be of a contact type and can thus be represented by a boundary condition satisfied by the polymer Green function. For contact interactions the boundary condition is independent of the local curvature, which need not be the case for more realistic polymer-surface interactions [5]. If \mathcal{N} refers to the number of beads of the polymer, then the Green function $G(\mathbf{R}, \mathbf{R}'; \mathcal{N})$ satisfies a diffusion-type equation [6]. The corresponding free energy can be written as

$$F = -kT \ln \Xi(\mathcal{N}) = -kT \ln \int d^3\mathbf{R} d^3\mathbf{R}' G(\mathbf{r}, \mathbf{R}'; \mathcal{N}), \quad (2)$$

where $\Xi(\mathcal{N})$ is the partition function of the polymeric chain. Since it proves convenient to work with Laplace-transformed quantities, we introduce them in the standard manner as, *e.g.*,

$$G(\mathbf{R}, \mathbf{R}'; \mathcal{N}) = \frac{1}{2\pi i} \int_{\mathcal{C}} ds \exp[s \mathcal{N}] G(\mathbf{R}, \mathbf{R}'; s),$$

and adopt the convention that all the quantities with the argument s relate to the Laplace transforms of the same quantities with the argument \mathcal{N} . The Laplace-transformed Green function thus satisfies [6]

$$[\nabla^2 - s] G(\mathbf{R}, \mathbf{R}'; s) = -\delta(\mathbf{R} - \mathbf{R}'), \quad (3)$$

where the spatial dimensions are now measured in units of $l/\sqrt{6}$, where l is the step length. The above equation has the form of the standard Helmholtz equation and its solution for infinite space (we designate it as $G_0(\mathbf{R}, \mathbf{R}'; s)$) is well known.

After these formal preliminaries we are ready to treat the case where the Green function

has to satisfy a boundary condition at the surface that has in the general case the form

$$\frac{\partial G(\mathbf{R}_\alpha, \mathbf{R}'; s)}{\partial n_\alpha} - \kappa G(\mathbf{R}_\alpha, \mathbf{R}'; s) = 0, \quad (4)$$

where κ is proportional to the strength of the polymer-surface interaction. In the above equation and in what follows we adopt the convention that all the coordinates with Greek indices relate to the bounding surface, thus \mathbf{R}_α stands for the radius vector \mathbf{R} on the bounding surface. The two limiting cases of the general boundary condition, viz. $\kappa > 0$ and $\kappa < 0$ with large enough $|\kappa|$, correspond to polymer steric exclusion and polymer adsorption to the surface. In fact, as can be shown quite straightforwardly, the limit $\kappa \rightarrow \infty$ corresponds exactly to the case of $G(\mathbf{R}_\alpha, \mathbf{R}'; s) = 0$, which is the standard surface steric-exclusion boundary condition.

Since we have reduced our problem to the solution of the Helmholtz equation with a mixed boundary condition at the bounding surface, we can use the method of multiple-scattering expansion [3] which has already proved useful in the study of the properties of electric double layers (in the Debye-Hückel approximation) near curved surfaces of arbitrary shape [3]. The Green function appropriate for the mixed-boundary-conditions problem, eq. (4), has been derived by Balian and Bloch (compare eq. (II.27) in the Balian-Bloch paper [3]) in the form of a convergent expansion in local curvature.

If we now insert their expression for the Green function into eq. (2), we get a series for the polymer partition function that can be effectively resummed in a very elegant manner by introducing an auxiliary function (F), as a double integral of the Green function over the half-space defined by the bounding surface (the same definition is used in Balian and Bloch [3]),

$$F(\mathbf{R}_\alpha, \mathbf{R}_\beta; s) = \int \int d^3\mathbf{R} d^3\mathbf{R}' G_0(\mathbf{R}, \mathbf{R}_\alpha; s) G_0(\mathbf{R}_\beta, \mathbf{R}'; s). \quad (5)$$

The resummed partition function can now be obtained in a very simplified form:

$$\Xi(s) = \Xi_0(s) + 2 \int dS_\alpha U(\mathbf{R}_\alpha, \mathbf{R}_\alpha; s) = \Xi_0(s) + 2 \text{Tr} U(\mathbf{R}_\alpha, \mathbf{R}_\beta; s), \quad (6)$$

where $\Xi_0(s) = \int \int d^3\mathbf{R} d^3\mathbf{R}' G_0(\mathbf{R}, \mathbf{R}'; s)$ and the surface part of the partition function (the second term in the above equation) can be written as a trace of the operator $U(\mathbf{R}_\alpha, \mathbf{R}_\beta; s)$ that satisfies an integral equation

$$U(\mathbf{R}_\alpha, \mathbf{R}_\beta; s) - 2 \int dS_\gamma U(\mathbf{R}_\alpha, \mathbf{R}_\gamma; s) \bar{\nabla}_\gamma G_0(\mathbf{R}_\gamma, \mathbf{R}_\beta; s) = \bar{\nabla}_\beta F(\mathbf{R}_\alpha, \mathbf{R}_\beta; s), \quad (7)$$

where $\bar{\nabla}_\gamma = \partial/\partial n_\gamma - \kappa$. One can immediately show, by perturbatively expanding the equation defining the function U , that for the cases $\kappa = 0$ and $\kappa \rightarrow \infty$, which in turn reduce to the Neumann and Dirichlet boundary conditions, the limiting results for the Green's function coincide exactly with those derived by Balian and Bloch in a different fashion.

We proceed now to the limiting cases announced in the introduction and corresponding to adsorption ($\kappa < 0$) and exclusion ($\kappa > 0$) of the polymer from the surface. For $|\kappa| \gg 1$ we have $\bar{\nabla}_\beta \rightarrow -\kappa$ in eq. (7), that can thus be solved perturbatively for U in different orders of the local curvature.

First of all we show how the local curvature of the bounding surface enters the equation

for U . We defined F as

$$\begin{aligned}
 F(\mathbf{R}_\alpha, \mathbf{R}_\beta; s) &= \int \int d^3\mathbf{R} d^3\mathbf{R}' G_0(\mathbf{R}, \mathbf{R}_\alpha; s) G_0(\mathbf{R}_\beta, \mathbf{R}'; s) = \\
 &= \frac{1}{s^2} \left[\frac{1}{4} - \frac{1}{2} \left(\int \frac{\partial G_0(\mathbf{R}_\gamma, \mathbf{R}_\alpha; s)}{\partial \mathbf{n}_\gamma} dS_\gamma + \int \frac{\partial G_0(\mathbf{R}_\gamma, \mathbf{R}_\beta; s)}{\partial \mathbf{n}_\gamma} dS_\gamma \right) + \right. \\
 &\quad \left. + \int \int \frac{\partial G_0(\mathbf{R}_\gamma, \mathbf{R}_\alpha; s)}{\partial \mathbf{n}_\gamma} \frac{\partial G_0(\mathbf{R}_\gamma, \mathbf{R}_\beta; s)}{\partial \mathbf{n}_\gamma} dS_\gamma dS_{\gamma'} \right]. \quad (8)
 \end{aligned}$$

While evaluating the surface integral following the application of the Gauss theorem to eq. (3) we have taken into account the fundamental discontinuity property of the Green function at the surface [3], *i.e.*

$$\frac{\partial G_0(\mathbf{R}_\gamma, \mathbf{R}_\alpha^+; s)}{\partial \mathbf{n}_\gamma} = \frac{\partial G_0(\mathbf{R}_\gamma, \mathbf{R}_\alpha; s)}{\partial \mathbf{n}_\gamma} + \frac{1}{2} \delta(\mathbf{R}_\gamma - \mathbf{R}_\alpha),$$

where \mathbf{R}_α^+ stands for the limit as \mathbf{R} approaches the bounding surface from the bulk.

$F(\mathbf{R}_\alpha, \mathbf{R}_\beta; s)$ now clearly has three terms of zero, first and second order in the normal derivative of the Green function at the bounding surface. The first term corresponds to the (unnormalized) probability that the chain is anywhere in the half-space defined by the bounding surface. The second term corresponds to the probability that the chain, going along the surface, arrives at the point \mathbf{R}_α (or \mathbf{R}_β), if it starts from any other point on the surface. The third term corresponds to the chain that touches the surface at two distinct positions (\mathbf{R}_α and \mathbf{R}_β) while going along the surface. It therefore corresponds to «in-plane bridging». That the normal derivative of the Green function can be expanded into a series with respect to the local curvature starting with a first-order term can be derived straightforwardly if we approximate the surface at the point \mathbf{R}_ω to its tangential plane. The equation of the bounding surface S in the frame of reference of the tangential plane is $z(x, y) \approx \approx (1/2)(x^2/R_1 + y^2/R_2) + \dots$, where R_1 and R_2 are the two principal radii of curvature at the point \mathbf{R}_ω on the surface. (x, y) present the projected deviations from this point onto the tangential plane. The calculations are performed by carrying out all the integrations with the point ω fixed, the integration with respect to ω being performed last [3].

Evaluating the normal derivative of the Green function on the tangential plane, one thus obtains (see ref. [3] for details)

$$\frac{\partial G_0(\mathbf{R}_\alpha, \mathbf{R}_\beta; s)}{\partial \mathbf{n}_\alpha} \approx - \frac{1}{2R_\omega} (\rho \nabla_\rho)^{(p)} G_0(\rho = |\mathbf{R}_\alpha - \mathbf{R}_\beta|).$$

The superscript (p) here and later on stands for the planar (zero curvature) approximation to the superscripted quantity. We note here that while deriving the expression for $\partial G_0(\mathbf{R}_\alpha, \mathbf{R}_\beta; s)/\partial \mathbf{n}_\alpha$ one averages over all the directions of the principal curvature axes. The next order term in the expansion of the normal derivative of the Green function is of the third order in local curvature. Since it is clear now that F can be expanded into a series with respect to the local curvature of the bounding surface, we develop all the quantities entering the equation defining the operator U in the same way. If $F^{(i)}$ for $i = 0, 1$ are simply the zero and the first-order curvature terms of the F function, then $F^{(2)}$ is somewhat more complicated, containing the second-order term of F as well as the second-order terms of the local surface

area element and the second-order term of the Green function (see Duplantier [3]) that enter the surface integral on the l.h.s. of eq. (7). The different orders $F^{(i)}$ are thus obtained in the form

$$\begin{cases} F^{(0)}(\mathbf{R}_\alpha, \mathbf{R}_\beta; s) = \frac{1}{4s^2}, \\ F^{(1)}(\mathbf{R}_\alpha, \mathbf{R}_\beta; s) = -\frac{1}{2s^2} \left[\int \frac{\partial G_0(\mathbf{R}_\gamma, \mathbf{R}_\alpha; s)}{\partial \mathbf{n}_\gamma} dS_\gamma^{(p)} + \int \frac{\partial G_0(\mathbf{R}_{\gamma'}, \mathbf{R}_\beta; s)}{\partial \mathbf{n}_{\gamma'}} dS_{\gamma'}^{(p)} \right], \\ F^{(2)}(\mathbf{R}_\alpha, \mathbf{R}_\beta; s) = \frac{1}{s^2} \iint \frac{\partial G_0(\mathbf{R}_\gamma, \mathbf{R}_\alpha; s)}{\partial \mathbf{n}_\gamma} \frac{\partial G_0(\mathbf{R}_{\gamma'}, \mathbf{R}_\beta; s)}{\partial \mathbf{n}_{\gamma'}} dS_\gamma^{(p)} dS_{\gamma'}^{(p)} + \\ + \int dS_\gamma^{(2)} U(\mathbf{R}_\alpha, \mathbf{R}_\gamma; s) G_0^{(p)}(\mathbf{R}_\gamma, \mathbf{R}_\beta; s) + \int dS_{\gamma'}^{(p)} U(\mathbf{R}_\alpha, \mathbf{R}_{\gamma'}; s) G_0^{(2)}(\mathbf{R}_{\gamma'}, \mathbf{R}_\beta; s), \end{cases} \quad (9)$$

where $dS^{(2)}$ is the second-order curvature term of the local surface area element ($dS \approx (1/2)(\nabla z)^2 dS^{(p)}$), while $G_0^{(2)}(\mathbf{R}_\gamma, \mathbf{R}_\beta; s)$ is the second-order curvature term in the expansion of the Green function in the coordinate system defined by its tangential plane,

$$G_0^{(p)}(\mathbf{R}_\gamma, \mathbf{R}_\beta; s) \approx \frac{1}{2} z_\gamma^2(x, y) \frac{\partial^2 G_0(\mathbf{R}_\gamma, \mathbf{R}_\beta; s)}{\partial z_\gamma^2}.$$

$F^{(2)}$ represents now the effective in-plane bridging term, with the second and the third terms in the last line of eq. (9) stemming from the curvature dependence of the kernel in eq. (7).

With these provisos we solve eq. (7) order by order in curvature ($U, i = 0, 1, 2$) and obtain simple expressions that we can use for the evaluation of the trace of U :

$$\begin{cases} U^{(0)}(\mathbf{R}_\alpha, \mathbf{R}_\alpha; s) = -\frac{\kappa}{4s^{3/2}(\kappa + s^{1/2})}, \\ U^{(1)}(\mathbf{R}_\alpha, \mathbf{R}_\alpha; s) = \frac{\kappa}{2R_\omega s^2(\kappa + s^{1/2})}, \\ U^{(2)}(\mathbf{R}_\alpha, \mathbf{R}_\alpha; s) = -\frac{\kappa}{s^{3/2}(\kappa + s^{1/2})} \left[\frac{1}{4R_\omega^2 s} - \frac{\kappa}{8s(\kappa + s^{1/2})} \left(\frac{1}{R_\omega^2} - \frac{1}{R_1 R_2} \right) \right]. \end{cases} \quad (10)$$

The partition function is now obtained in the form

$$\Xi(\mathcal{N}) = \mathcal{L}^{-1}[\Xi(s)] = \mathcal{L}^{-1} \left[\Xi_0(s) + 2 \int dS_\omega \sum_{i=0}^2 U^{(i)}(\mathbf{R}_\omega, \mathbf{R}_\omega; s) \right]. \quad (11)$$

The inverse Laplace transforms (designated by \mathcal{L}^{-1}) depend crucially on the sign of κ . For $\kappa > 0$ the spectrum of U has no bound states and an expansion in series with respect to κ^{-1} is possible. On the other hand, for $\kappa < 0$ the presence of bound states in the spectrum of U prevents a simple expansion in terms of κ^{-1} . For the polymer sterically excluded from the vicinity of the surface the main contribution to the partition function comes from the bulk part that scales as volume, while for the polymer adsorbed to the surface the main

contribution to the partition function is the adsorption part that scales as the surface area. Bearing this in mind, we are led to the following form of the free energy for the case of surface-excluded polymer:

$$\mathcal{F}(\kappa > 0) = \mathcal{F}_0 + \left(\frac{\mathcal{N}}{V} \right) \frac{l^2 kT}{6\pi^{1/2} \langle R^2 \rangle^{1/2}} \int dS_\omega - \left(\frac{\mathcal{N}}{V} \right) \frac{l^2 kT}{6} \int dS_\omega \frac{1}{R_\omega} +$$

$$+ \left(\frac{\mathcal{N}}{V} \right) \frac{l^2 kT \langle R^2 \rangle^{1/2}}{18\pi^{1/2}} \int dS_\omega \left(\frac{1}{R_\omega^2} + \frac{1}{R_1 R_2} \right) - \dots, \quad (12)$$

where $\mathcal{F}_0 = -kT \ln \int d^3 R$, $\langle R^2 \rangle = \mathcal{N} l^2$ and \mathcal{N}/V is the monomer volume concentration. The case of the adsorbed polymer leads in its turn to the following form of the free energy:

$$\mathcal{F}(\kappa < 0) = \mathcal{F}_0 + \left(\frac{\mathcal{N}}{S} \right) \frac{l^2 kT}{12|\kappa| \langle R^2 \rangle} \int dS_\omega \frac{1}{R_\omega} - \left(\frac{\mathcal{N}}{S} \right) \frac{l^2 kT}{6} \int dS_\omega \left(\frac{1}{R_\omega^2} - \frac{1}{R_1 R_2} \right) + \dots, \quad (13)$$

where here

$$\mathcal{F}_0 = -kT \ln \frac{\exp \left[\frac{\kappa^2 l^2 \mathcal{N}}{6} \right] \int dS_\omega}{|\kappa|} \approx -kT \frac{\kappa^2 l^2}{6} \left(\frac{\mathcal{N}}{S} \right) \int dS_\omega$$

is the part of the free energy corresponding to the surface-bound polymer partition function [4] with surface monomer concentration equal to \mathcal{N}/S , where $S = \int dS_\omega$ is the total surface area. While deriving the above expressions for the free energy we implicitly assumed the $\mathcal{N} \gg 1$ limit.

We recognize that the Gaussian-curvature term has the same sign for both extremes of κ values, while the signs of the first- and second-order mean curvature terms alternate for different signs of κ . Since, as far as topology of the surface is concerned, the minimal value of the integral $\int dS (1/R_\omega^2)$ also increases with the genus of the surface, one can conclude that the adsorbing polymer will favor proliferation of handles. A general conclusion of this type cannot be drawn for the surface-excluded polymer.

The surface adsorption/exclusion act, however, quite differently on the renormalization of the elastic constant (K_c)—a consequence of the in-plane bridging of the polymeric chain along the curved surface. The steric exclusion of the polymeric chain from the vicinity of the surface stiffens the bounding surface, while the adsorption makes it prone to bending, in general agreement with the conclusions by Brooks *et al.* [2]. This should lead to pronounced modifications in the interaction of two flexible surfaces with polymers in between. The adsorbing polymer should in this case promote bridging attraction [7] between the surfaces as well as curvature destabilisation of the interacting surfaces. (The same twofold action, but with signs reversed, was shown to exist also for screened electrostatic interactions [8].) Such curvature instability has been predicted quite some time ago on very general grounds [9] and is bound to play a decisive role in the vesicle shape transformations [1].

Similarly the linear curvature term that renormalizes the spontaneous curvature in eq. (1) prefers bends towards the polymer-rich phase in the case of adsorption interactions, while the exclusion favours bending away from the polymer phase. Localized weak adsorption of a polymer to a closed vesicle would thus severely affect its equilibrium shape through the coupling between adsorption and bending.

The formal method presented here for assessing the effect of the polymer-boundary

interactions on the elastic properties of the bounding surface is more general than those used recently in the treatment of similar problems [2]. Its drawback lies in the fact that it can be applied only to linear problems. Polymer-polymer interactions (as, *e.g.*, excluded volume), that have been recently dealt with in the framework of the Cahn-de Gennes and scaling theories [2], can be included into the present linear theory through the use of variational principles that preserve the linearity of the Green's function equation but nevertheless include also the effects of the polymer-bulk interactions. Also, the method presented here, being complementary to other approaches [2], can be straightforwardly generalized to persistent polymeric chains or to other polymer models for that matter, that can be described in the framework of a Green's function formalism.

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The author is grateful to Prof. B. DUPLANTIER for pointing out the limits of the assertion (contained in an earlier version of the MS) that surface interacting polymer always favours proliferation of handles. Indeed, in the case of surface-excluded polymer, this can be shown only for the two lowest genus, while for higher ones one does not really know.

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